

REMARKS

Claim Status

Claims 1-5 and 12-16 are pending in this application, of which claims 1, 6, 12, 17 and 21 are independent and claims 6-11 and 17-21 have been withdrawn.

Claims 1 and 12 have been amended to correct informalities in the claim language and to more clearly define the present subject matter. No new matter has been added.

Patentability under 35 U.S.C. § 103

Claims 1, 12 and 14 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Sung (US 2005/0019114) and further in view of Meng (US 2003/0039603). Claims 2, 3, 13 and 14 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Sung and Meng, and further in view of Swain (US 2006/0110024). Claims 4, 5, 15 and 16 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Sung and Meng or Sung and Swain, and further in view of Akaishi (WO 2004/046062). Claims 15 and 16 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Sung and Meng or Sung and Meng in view of Swain, and further in view of Akaishi. Applicant respectfully traverses these rejections for at least the following reasons.

Applicant respectfully submits that, at a minimum, none of the cited references disclose or even suggest that “a particle of said diamond includes at least 100 ppm and at most 1,000 ppm of boron as a solid solution,” as recited by claim 1 or “a particle of said diamond includes at least 1,000 ppm and at most 100,000 ppm of boron as a solid solution,” as recited by claim 12.

On page 2 of the instant Office Action, the Examiner asserted that it is expected that when using an amount of starting material [of Meng], without otherwise converting or removing the compound, the same amount should be present in the final product [of Meng].

Applicant submits, however, that the amount of starting material is not necessarily maintained in the final product. For example, as shown in “High-pressure synthesis of high-purity diamond crystal” (Sumiya et al.) attached hereto, even if the boron is included in the source carbon material, the amount of born in the diamond would be only about 1/100 of the amount in the source carbon. On page 1362, the section “3.2 Boron impurity” of the above document describes that when the carbon source contained about 30 ppm boron, the boron concentration in the diamond was about 0.3 ppm and that the carbon source contained about 1-2 % of boron, the boron concentration in the diamond was about 3-30 ppm. As such, the Examiner’s assertion as set forth above has no technical basis and has no merit.

Further, it appears that the amount of boron in Meng would be at most 50 ppm or less, and there is no motivation or suggestion to increase the amount of boron in the diamond. As shown in “Effect of the additive boron on diamond crystals synthesized in the system of Fe-based alloy and carbon at HPHT” (Zhang, et al.) attached hereto, with increasing of the content of boron, the color of crystals becomes darker (see, page 286 of Zhang). Zhang also describes that when the amount of boron in the source exceeds 0.5 wt%, the crystal becomes imperfect (see, page 286 of Zhang). It is noted that in view of Sumiya, the amount of boron in the diamond of Zhang would be about 50 ppm when the amount of boron in the source is 0.5 wt%. Further, Meng discloses at paragraph [0017] as follows:

“The presence of N prevents the incorporation of B into the diamond structure, resulting in B being present as an impurity inclusion and consenquently diamond crystals of black color. The novel boron doped, blue diamond has less B as an impurity inclusion than that of black color diamond.”

In addition, Sumiya discloses that when the boron amount in the diamond is 3-30 ppm, blue diamond was obtained (see, page 1362 of Sumiya). Accordingly, in view of Sumiya and Zhang, the blue diamond of Meng would contain at most 50 ppm of boron. Further, as disclosed in paragraph [0017], Meng teaches away from adding more boron to obtain blue diamond.

Based on the foregoing, claims 1 and 12 and all claims dependent thereon are patentable over the cited references. Applicant requests that the Examiner withdraw the rejections of the claims under 35 U.S.C. § 103.

CONCLUSION

Having fully responded to all matters raised in the Office Action, Applicant submits that all claims are in condition for allowance, an indication for which is respectfully solicited. If there are any outstanding issues that might be resolved by an interview or an Examiner's amendment, the Examiner is requested to call Applicant's attorney at the telephone number shown below.

To the extent necessary, a petition for an extension of time under 37 C.F.R. 1.136 is hereby made. Please charge any shortage in fees due in connection with the filing of this paper, including extension of time fees, to Deposit Account 500417 and please credit any excess fees to such deposit account.

Respectfully submitted,

McDERMOTT WILL & EMERY LLP



Takashi Saito
Limited Recognition No. L0123

600 13th Street, N.W.
Washington, DC 20005-3096
Phone: 202.756.8000 TS/MaM
Facsimile: 202.756.8087
Date: December 14, 2011

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Effects of the additive boron on diamond crystals synthesized in the system of Fe-based alloy and carbon at HPHT

J.Q. Zhang ^a, H.A. Ma ^a, Y.P. Jiang ^a, Z.Z. Liang ^a, Y. Tian ^a, X. Jia ^{a,b,*}^a National Lab of Superhard Materials, Jilin University, Changchun 130012, China^b Henan Polytechnic University, Jiaozuo 454000, ChinaReceived 1 November 2005; received in revised form 25 May 2006; accepted 24 June 2006
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Abstract

In this paper, the boron-doped diamond crystals were synthesized at high pressure and high temperature (HPHT) by adding amorphous boron to the system of carbon and Fe-based solvent/catalyst. The effects of the additive boron on the properties of the synthesized diamond crystals, especially, on the growth process and the morphology of diamonds, have been extensively studied. We found that the integrity of diamond crystals synthesized at optimal growth condition and the growth region of particular morphology changed with increasing of the content of additive boron. It is found that the growth region of {111} face becomes wider, and that of {100} face becomes narrower and almost disappears with the increasing boron concentrations. The surface morphology of boron-doped diamonds were detected with scanning electron microscope (SEM), and we found a great deal of defects on {111} face when the content of additive boron increased to 0.25 wt.%. The results of X-ray photoelectron spectroscopy (XPS) on the surface of diamond show that boron lies on the surface of diamonds and bonds with C and O, respectively. We proposed a model of bald-point to explain these experimental observations.

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Keywords: Boron; Dope; Additive; Diamond; HPHT

1. Introduction

Pure and doped diamonds have attracted much technological attention because of the high carrier mobility, high thermal conductivity, high breakdown field, low dielectric constant, and wide band gap. For example, pure diamond is an insulator with a band-gap of 5.45 eV, and its heat conductivity is much better than copper's. Furthermore, diamond can stand a very high electric field [1–3]. In order to apply diamond to electric fields such as micro electron contrasts, electrode emission poles, optical detector, and transistors [4–8], it is very important to fabricate low-resistivity *n*-type and *p*-type materials by doping diamond with donor and acceptor impurities respectively.

As a representative acceptor in *p*-type diamond, small B atoms can be incorporated substitutionally into diamond with

high reproducibility and high enough concentration to be useful for electronic devices [9]. Recently, B-doped diamond was found to be a superconductor with a critical temperature (T_c) of 2.3 K [10]. Additional confirmation has also been provided recently by Sidorov et al. [11]. This observation is a breakthrough finding, not only due to the obvious practical implications, but also of the scientific importance.

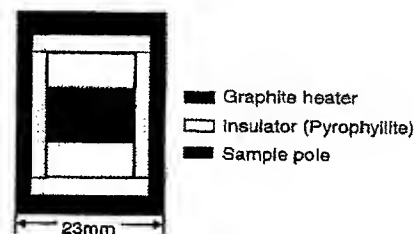


Fig. 1. Sample assembly sketch for high pressure experiment.

* Corresponding author: National Lab of Superhard Materials, Jilin University, Changchun 130012, China. Fax: +86 431 5168858.
E-mail address: jiaxp@jlu.edu.cn (X. Jia).

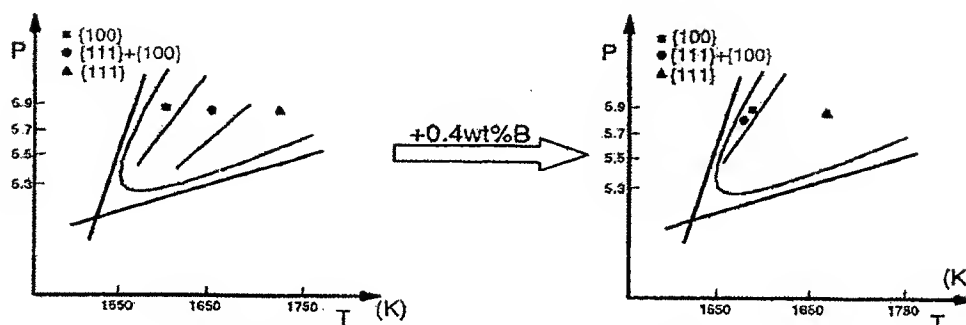


Fig. 2. Growing regions of every crystal face after adding boron.

Experimentally, many studies have been concentrated on the fabrication of boron-doped diamond film [12–15], but there is little study about the HPHT synthesis of boron-doped diamond single crystals. In this paper, we added amorphous boron to the system of powder graphite and solvent/catalyst to synthesize boron-doped diamond crystals at HPHT. The virtue of this method is that we can change the content of boron additive in the growth system freely, and observe the effects on the properties of boron-doped diamond in the carbon solvent/catalyst system. The effects of the additive boron on the growth process and the morphology of diamond crystals have been studied. The model of bald-point is proposed to explain these experimental phenomena.

2. Experimental

The experiments were carried out in a cubic anvil high pressure and high temperature apparatus (SPD-6 × 1200). Graphite powder, Fe₉₀Ni₁₀ catalyst powder and amorphous boron powder were used in the experiments. Firstly we sufficiently mixed the powder of boron, graphite and catalyst for 6 h. The content of additive boron in the mixed-powder is in the range of 0.1 wt.% to 0.5 wt.%. Then the mixed-powder was pre-pressed to a sample disk. The sample assembly for synthesis was shown in Fig. 1. The synthetic conditions were 5.4 GPa–5.6 GPa and 1550 K–1700 K. The pressure was calibrated by the pressure-induced phase transitions of bismuth, thallium, and barium. The

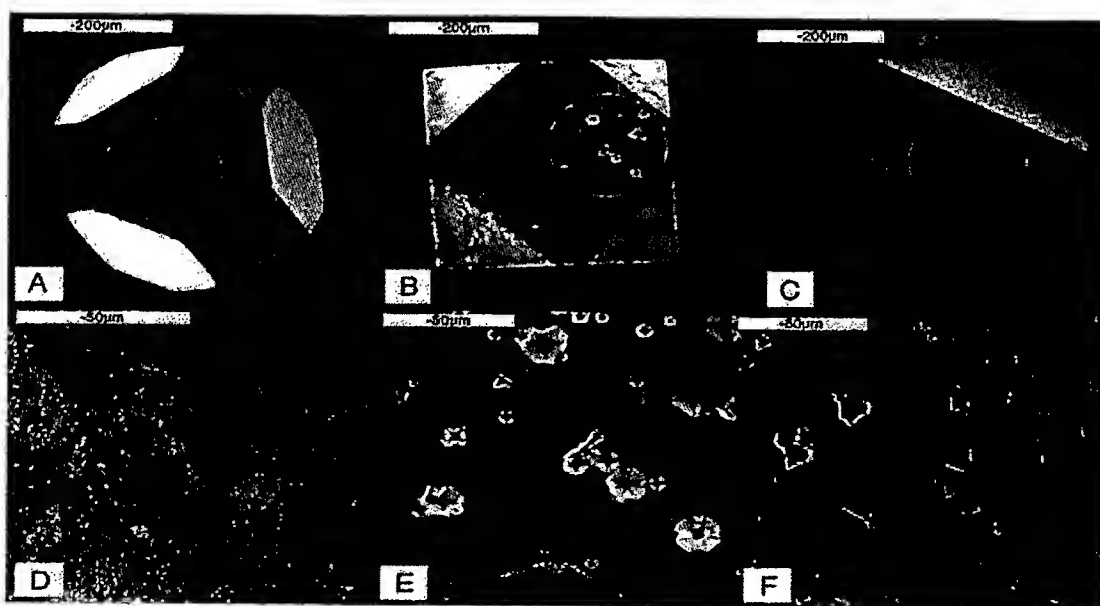


Fig. 3. SEM of diamond (A, B and C are the diamonds synthesized with 0 wt.%, 0.1 wt.% and 0.25 wt.% additive boron, respectively, and D, E and F are the amplification of A, B and C, respectively).



Fig. 4. The imperfect crystals of diamond synthesized with 0.5 wt.% additive boron.

temperature was measured by the Pt6%Rh–Pt30%Rh thermocouple [16].

After the HPHT experiment, graphite and metal film on the surface of diamond crystals were removed by boiling in strong acid. The surface morphology was observed by optical mi-

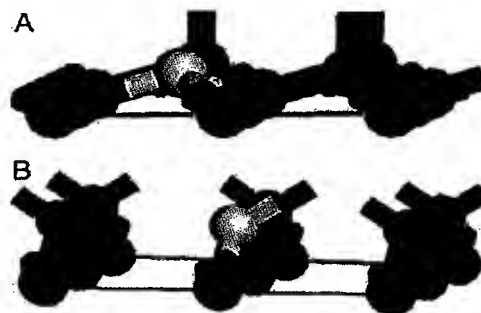


Fig. 6. Substitution of boron atom for carbon atom on the {111} and the {100} surface of diamond (the pale are carbon atoms, the dark is boron atom). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

croscope and scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) was used to detect the state of boron on the surface of diamond.

3. Results and discussion

3.1. The effects of additive boron on the synthetic diamond

3.1.1. The effects of additive boron on the growth regions of diamond

During the experiments, we continuously increased the content of additive boron in the sample disk, and found that the growth region of {111} face became wider while the region of {100} face became narrower. It should be pointed out that when boron concentration was increased up to 0.4 wt.% in the sample disk, the growth region of {100} face almost disappeared even at very high pressure as shown in Fig. 2. The morphological changes observed in this experiment were in a good agreement with two previous experimental works about the B-doped CVD diamond film. They also suggested that the {111} face tends to predominate with increasing boron concentrations [17,18].

3.1.2. The surface morphology of boron-doped diamond

In order to probe the surface morphological changes in the synthesized diamond crystals, we used the SEM technique to detect the surfaces of the crystals with different boron concentrations in the sample disk of 0 wt.%, 0.1 wt.%, and 0.25 wt.%, respectively. It was observed that the surfaces of the pure diamond crystals exhibited some striations and few small pits in the {111} face as indicated in Fig. 3(A) and (D). On the contrast, the surfaces of the boron-doped diamond crystals with the boron content of 0.1 wt.% still show some striations, while one could clearly observe many big pits with the shape of down pyramid on the {100} face as shown in Fig. 3(B) and (E). Note that when boron was increased up to 0.25 wt.% in the sample disk, the striations disappear, instead many triangular or triangle-like pits occupy the surface in the {111} face as shown in Fig. 3(C) and (F). It should be also noted that the diamonds in Fig. 3(A), (B), and (C) were synthesized at the conditions of 5.6 GPa and

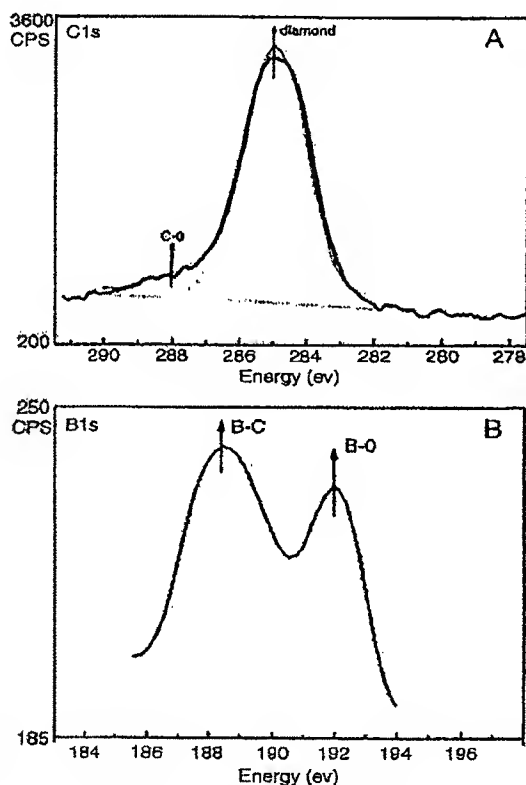


Fig. 5. XPS of diamond (A and B are C1's peak and B1's peak, respectively).

1610 K, 5.5 GPa and 1590 K, and 5.5 GPa and 1610 K, respectively.

With increasing of the content of additive boron, the color of crystals becomes darker, and the crystal tends to be imperfect even at the conditions of growing high-quality pure diamonds. As shown in Fig. 4, all the crystals were nearly imperfect crystals when the content of boron in the sample disk was increased up to 0.5 wt.%.

3.1.3. XPS of boron-doped diamond

We also used XPS to detect the surface of boron-doped diamond. The XPS for the boron-doped diamond with the boron content of 0.25 wt.% was shown in Fig. 5. From the XPS for carbon atoms as shown in Fig. 5(A), it is clear that there are mainly two types of chemical bonding of C–C and C–O on the surface of the crystals with the binding energies of 285.1 and 288.1 eV, respectively. Fig. 5(B) shows the XPS results for boron atoms. Two types bonding characters are also observed as B–C and B–O bonds with the binding energies of 188.7 and 192.6 eV, respectively. Note that the binding energy for B–C bond of 188.7 eV is smaller than that (186.8 eV) of B_4C . Thus, it is suggested that the B–C bonding behavior in the studied boron-doped diamond crystal is different with that in the perfect crystal of B_4C . The process of synthesis and disposal are exposed to air. As a consequence, oxygen will inevitably incorporate into the boron-doped diamond. Oxygen has a strong electronegativity and can easily react with other cations. Therefore, the introduction of oxygen in the doped diamond will result in the C–O and B–O bonds.

3.2. The model of bald-point for explaining the experimental results

We design a model to explain the experimental results. On the {111} face of diamond as shown in Fig. 6(A), one carbon atom bonds with three nearest carbon atoms, and thus there exists one dangling bond. However, on the {100} face as shown in Fig. 6(B), one carbon atom bonds with two nearest carbon atoms, while two dangling bonds are left.

On the {111} face, when boron was doped into the diamond, one boron atom substitutes one carbon atom. Since boron atom only has three valence electrons, there is no dangling bond on the boron atom (Fig. 6A). Thus, on the {111} face, as the crystal grows, it is hard for new carbon atoms to bond with the doped boron atoms. The lattice sites where boron atoms substitute carbon atoms will become bald-points in the growth process. However, when boron atoms substitute carbon atoms on {100} face, one boron atom bonds with two nearest carbon atoms, and, thus, one dangling bond remains (Fig. 6B). So the boron atoms can react with new carbon atom as the crystal grows. The bald-points on {111} face will influence transportation and lattice of carbon atoms in this direction. Therefore, the growth rate along the $\langle 111 \rangle$ direction decreases and as a consequence the integrity of crystal decreases. It is noteworthy that the growth rate along the $\langle 100 \rangle$ direction is faster than that along the $\langle 111 \rangle$ direction when boron was doped into diamond. When the content of boron in the sample disk increases, the number of

bald-points will increase and the growth rate along the $\langle 100 \rangle$ direction will be faster. When the growth rate along one direction is faster than the other directions, the crystal face corresponding to that direction will disappear firstly [19]. Thus when the boron additive was increased to 0.4 wt.%, the {100} face disappears and only {111} faces remained.

On the {111} face of diamonds grown from sample disk with 0.25 wt.% boron additive, there will be a great deal of defects. Since the iron is the major ingredient in the catalyst, we can regard the solubility of boron and carbon in iron as the analogy of the solubility in catalyst. According to the phase diagram of Fe–B and Fe–C system under normal pressure [20], the solubility of boron and carbon in iron is about 5 wt.% at normal pressure and high temperatures of 1500–1700 K. We can deduce that the solubility of boron and carbon in iron has the same magnitude under high pressure. Therefore, there will be excessive bald-points on the surface of diamond, and most of the bald-points will appear on the {111} face. These bald-points result in a great deal of defects on the {111} face.

When the additive boron in a sample disk exceeds 0.4 wt.%, the character of catalyst will change, and only {111} face remained. When additive boron exceeds 0.5 wt.%, not only the character of catalyst but also the V-shape growth region of diamond will change. More and more bald-points will form on the {111} face with the growing of the crystals. The bald-points may completely destroy the lattice of carbon atoms and the growth of diamond, and result in a great deal of skeleton crystals.

4. Conclusion

As the content of additive boron in sample disk increases, the growth region of the {111} face becomes wider, whereas the growth region of {100} face becomes narrower and nearly disappears. The percentage of high-quality crystal decreases continually and eventually all diamonds become skeleton crystals. The surface morphology of the diamond changes because of the additive boron. When the sample disk contains 0.25 wt.% additive boron, there will exist lots of triangular pits in the synthesized diamond. The bald-point model explains how the boron atoms are doped into the diamond, which will help us to understand the behaviors of boron in the diamond.

Acknowledgment

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**DIAMOND
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High-pressure synthesis of high-purity diamond crystal

H. Sumiya, S. Satoh

Itami Research Laboratories, Sumitomo Electric Industries Ltd., 1-1-1, Koyakita, Itami, Hyogo 664, Japan

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Abstract

High-purity type IIa diamond crystals of weight 1–2 carats, containing less than 0.1 ppm chemical impurities and few inclusions, have been successfully synthesized by a temperature gradient method at high pressures and temperatures. The concentration of nitrogen impurities in the diamond crystals was reduced to less than 0.1 ppm by adding an element of the IVA group to the solvent as a nitrogen getter. The boron impurity concentration was reduced to less than 0.1 ppm by using a high-purity graphite (<1 ppm impurities) as the carbon source. Nickel impurities were avoided by using an Fe–Co alloy system for the solvent. Furthermore, by adding elements which can reduce the formation of carbides such as TiC or ZrC in the solvent, inclusions of the carbide or the solvent metal in the diamond crystal were substantially decreased, and consequently good-quality type IIa diamond crystals were obtained even at a growth rate as high as 2–3 mg h⁻¹.

Keywords: Crystal growth; High pressure/high temperature; Impurities; Synthetic diamond

1. Introduction

Synthetic diamond crystals several millimeters in size, grown by the temperature gradient method (reconstitution technique) at high pressures and temperatures, are used in heat sinks, high-reliability cutting tools, wire drawing dies, TAB bonding tools and so on.

These conventional commercialized synthetic diamond crystals usually include nitrogen, boron and nickel as chemical impurities. Nitrogen is the most common impurity in synthetic diamonds. If nitrogen is present in the diamond growth environment, it is easily included in the lattice of the growing crystal. Nitrogen is also the principal impurity in natural diamonds. Depending on the nitrogen content and the form in which it is present, diamonds are classified into four types: Ia, Ib, IIa and IIb. Conventional diamonds synthesized under high pressure, which contain nitrogen in the form of isolated substitutional impurities, are classified as type Ib. Synthetic diamond powder, which has been produced industrially for many years for use as abrasive grit or polishing powder, is also type Ib. High-purity diamonds, which contain almost no nitrogen, are classified as type IIa.

The sources of nitrogen in synthetic diamond are the nitrogen impurities in the solvent metal and carbon source material, as well as the nitrogen in the gas in the

empty spaces or pores in the specimen chamber components. This nitrogen dissolves in the solvent metal and are incorporated in the diamond crystal during growth. The amount of nitrogen incorporated in the crystal differs depending on the type of solvent used, the synthesis temperature and other factors, but it generally ranges from several tens to 200 ppm. Because of these nitrogen impurities, the crystals have a yellowish tint and some of their properties are affected. In the optical spectrum, the absorption band due to the nitrogen impurities appears in the IR and UV regions. The nitrogen concentration in the grown diamonds can be reduced by adding a nitrogen getter (e.g. Al, Ti) to the solvent metal [1–3]. When the nitrogen concentration is decreased to about 0.1 ppm or less, the diamond crystals lose the visible yellow coloration, and the absorption bands due to the nitrogen impurity become undetectable. However, when a nitrogen getter is added to the solvent metal, metal inclusions tend to be trapped easily in the diamond crystal. In order to suppress incorporation of metal inclusions, the diamond crystals must be grown at a lower rate compared with that used in the absence of a nitrogen getter. It has been found that, although a type Ib diamond containing about 10–100 ppm dispersed nitrogen impurities can be grown at a rate of 2.5 mg h⁻¹, the growth rate of a type IIa diamond with a nitrogen concentration of less than 1 ppm has to be

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restricted to less than 1.5 mg h^{-1} to avoid the formation of metal inclusions [2].

It is well known that boron and nickel are also incorporated into the diamond crystal as chemical impurities. When a few micrograms of boron are added to the solvent metal or carbon source material, blue semi-conducting diamonds are grown [2-6]. The boron is incorporated in the diamond crystal lattice as an isolated substitutional impurity. In addition, when nickel or a nickel alloy is used as solvent metal, nickel atoms are also included in the diamond lattice [7-9]. Absorption bands due to these boron or nickel impurities also appear in the UV and IR regions of the spectrum of synthetic diamond. These absorption bands become sharper when the nitrogen impurities are reduced. Boron, in particular, is easily incorporated in the diamond crystal. Therefore, when the carbon source material or solvent metal contains boron impurities, even at concentrations as low as a few ppm, the diamond crystals become pale blue and exhibit sharp absorption bands.

There are very few reports of systematic investigations of the removal of these impurities. In this paper we describe the results of an investigation of a method of eliminating such chemical impurities and avoiding the incorporation of metal inclusions. The aim of this work was to synthesize high-purity type IIa diamond crystals, which are colorless and transparent, contain few chemical impurities and are substantially free from metal inclusions, without needing to reduce the growth rate.

2. Experimental method

Diamond crystals were grown by the temperature gradient method as shown in Fig. 1 using a belt-type high-pressure apparatus. The growth conditions were as follows: pressure, about 5.5 GPa; temperature, 1350°C . The growth rate was varied from 1 to 5 mg h^{-1} by changing the temperature difference between the carbon source and the seed crystal. The various temperature differences were set by adjusting the thickness of the solvent or the temperature gradient.

High-purity graphite containing less than 1 ppm

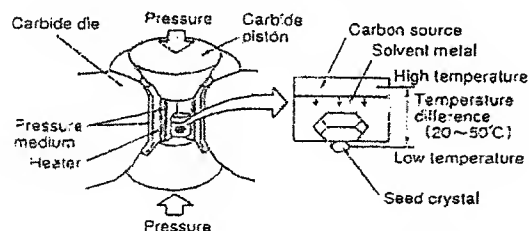


Fig. 1. Reaction cell for diamond growth (temperature gradient method).

boron and less than 10 ppm nitrogen was used as the carbon source material. Various commercial synthetic diamond powders, containing several ppm boron and about 200 ppm nitrogen, were also used as carbon source materials for comparison. High-purity Fe + Co alloys containing less than 1 ppm boron were used as solvent metals. The boron impurity content in the carbon source materials and solvent metals was measured by ICP spectrometry, and the nitrogen impurity content in the carbon source materials was determined by a titration method. Small synthetic diamond crystals for abrasive grits (size about 0.5 mm), grown by the phase difference mechanism (film growth), were used as seed crystals. A group IVa element (Ti, Zr or Hf) was added to the solvent metal as a nitrogen getter. Copper was added to the solvent metal in order to reduce the formation of carbides such as TiC or ZrC. The amounts of nitrogen getter and copper added to the solvent metal ranged from 0.5 to 10 wt.%. Aluminum was also examined as a nitrogen getter.

The concentrations of impurities such as nitrogen or boron in the diamond crystals were estimated from the IR and UV absorption spectra. The quantitative analysis of nitrogen and boron was performed using ESR and SIMS. The content of metal inclusions in the crystals was determined using a magnetic balance. Impurities produced in the solvent metal after diamond synthesis were analyzed using X-ray diffraction and EPMA.

When the nitrogen impurity exceeds a few ppm, the nitrogen concentration in the synthetic diamond crystal can be estimated from the absorption coefficient at 1130 cm^{-1} [10,11], but this band is not detectable in nitrogen concentrations less than about 1 ppm. The absorption coefficient at 270 nm (4.6 eV), which is a factor of several tens greater than the absorption coefficient at 1130 cm^{-1} , was used to determine the small concentration of nitrogen in the synthetic diamond. From an investigation of the relationship between the absorption coefficients at 270 nm and the nitrogen concentrations estimated from the intensity of an ESR signal, we obtained the proportional relation

$$N = 0.56\alpha \quad (1)$$

where N (ppm) is the nitrogen concentration in the synthetic diamond estimated from the ESR signal and α (cm^{-1}) is the absorption coefficient at 270 nm on the base of the tail-line. This result is consistent with the data reported by Chrenko et al. [10].

3. Results and discussion

3.1. Nitrogen impurity

First, the residual nitrogen contents were investigated in various diamonds synthesized using a variety of

elements as the nitrogen getter in an attempt to establish the efficiency of each. Several diamond crystals of weight about 1 carat were synthesized at a growth rate of 2 mg h^{-1} by adding various nitrogen getters to the solvent metal. Fe+40Co alloy was used as the solvent metal and the carbon source was high-purity graphite. The nitrogen content in the diamond crystals was estimated from Eqn. (1) based on the UV absorption coefficients at 270 nm.

Typical results obtained using Al and Ti as nitrogen getters are shown in Fig. 2. The nitrogen concentrations in the crystals decrease with increasing Al or Ti content added to the solvent. However, even when large amounts of Al are added, a small amount of nitrogen (several ppm) remains in the crystals and it is difficult to achieve a purity level of less than 1 ppm nitrogen. We believe that, although Al reacts with nitrogen in the solvent to form nitrides, decomposition also occurs, causing some of the nitrides to break down into Al and nitrogen. Ti is a more efficient nitrogen getter than Al, with almost all the nitrogen being removed when just a small amount of Ti is added to the solvent. Fig. 3 shows the UV spectra of diamond synthesized with the addition of different amounts of Ti. At 1.5 wt.% Ti, the absorption at 270 nm was not observed and the amount of the nitrogen was estimated at less than 0.1 ppm from ESR data. We believe that, unlike Al, Ti nitrides are not easily decomposed. Zr and Hf, which are also group IVA elements, showed the same effect as Ti.

To investigate the dependence of the composition of the solvent metal on the nitrogen removal rate, several diamonds were grown with Fe + Co alloys with various Co contents, and the nitrogen concentrations of the grown diamonds were measured as described above. The amount of Ti added was fixed at 1.5 wt.%. The results are shown in Fig. 4(a). The nitrogen concentrations in

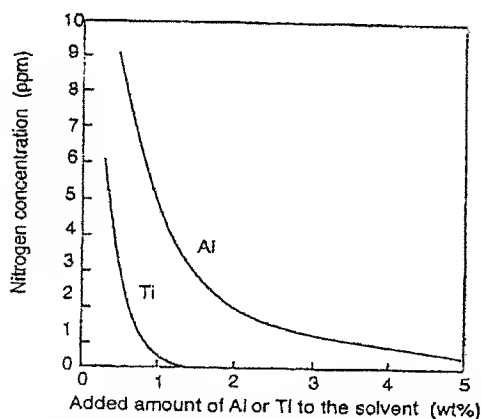


Fig. 2. Nitrogen concentration of diamond grown with Al or Ti added as the nitrogen getter.

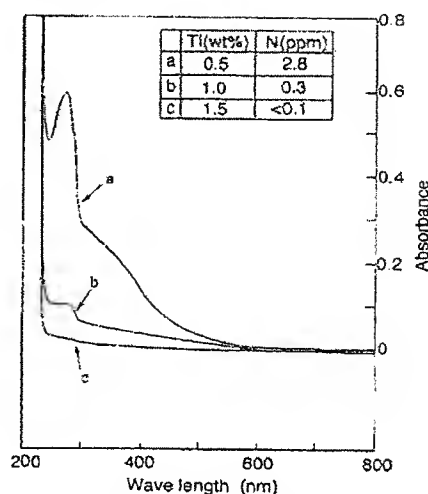


Fig. 3. Absorption spectra in the visible and UV regions for synthetic diamonds grown with Ti additions of (a) 0.5 wt.%, (b) 1.0 wt.% and (c) 1.5 wt.%. The nitrogen concentrations are estimated as (a) 2.8 ppm, (b) 0.3 ppm and (c) <0.1 ppm.

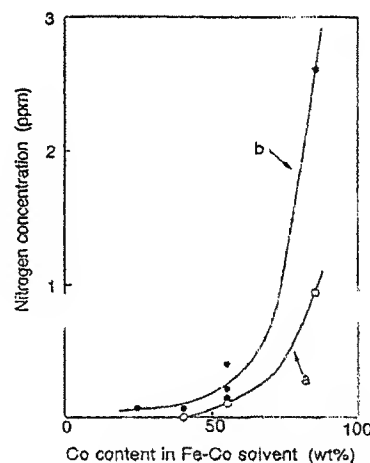


Fig. 4. Nitrogen concentration in diamond versus the Co content of Fe + Co solvent. The diamonds were grown with 1.5 wt.% Ti addition using (a) high-purity graphite and (b) synthetic diamond powder.

diamonds increases with increasing Co content in Fe + Co. This results indicates that the affinity of Co with nitrogen may be lower than that of Fe. Therefore the amount of nitrogen getter added must be changed depending on the composition of the Fe + Co solvent in order to remove nitrogen in the same way. For example, when Fe+55Co is used for the solvent, at least 2.5 wt.% Ti must be added to remove nitrogen completely.

Fig. 4(b) shows the results for the case where synthetic

diamond powder was used for the carbon source instead of high-purity graphite. The residual nitrogen concentrations are more than three times as high as when high-purity graphite is used as the carbon source because of the large amount of nitrogen impurity (about 200 ppm) in the synthetic diamond powder. Therefore the amount of nitrogen getter added must also be adjusted in proportion to the nitrogen content of the carbon source material.

According to these results, in order to remove the nitrogen impurity effectively it is preferable to decrease the Co content of the Fe+Co solvent metal and to increase the amount of Ti added. However, when the Co content is reduced too much or excessive nitrogen getter is added, inclusions are readily formed in the diamond crystal. According to the results of our investigations, it is preferable that the Co content of solvent metal is between 40 and 50 wt.%, and the amount of Ti added is 1.5-2 wt.%.

3.2. Boron impurity

Since the solvent metal does not include nickel, the grown diamonds contain few nickel impurities; no absorption band associated with nickel can be observed in the diamonds. However, a small absorption band due to boron was occasionally detected in the IR region. When commercial synthetic diamond powders were used as the carbon source, every grown diamond crystal was light blue in color and was an electrical conductor. Various synthetic diamond powders were analyzed and found to contain 3-30 ppm of boron. The origin of the boron in the grown diamond seems to be the boron impurity in the carbon source material.

In order to clarify how much of the boron in the carbon source might be incorporated in the diamond crystal, we grew several diamonds using various

synthetic diamond powders and measured the boron concentrations in the grown diamonds. As with nitrogen, the incorporation of boron varies with the growth sector: the take-up rate is much higher in the (111) sectors than in the other sectors [5]. Therefore the analysis of the boron concentrations in the grown diamonds was carried out in the (111) sectors. The boron concentrations measured by SIMS and FT-IR microscopic spectroscopy in the (111) sectors are shown in Fig. 5. In the diamond crystal grown from a carbon source containing about 5 ppm boron (Fig. 5(b)), the boron concentration is about 0.1 ppm and an absorption band near 2800 cm^{-1} can be observed. The absorption is associated with transitions between the ground state and the second or third excited states [12]. When the carbon source contained about 30 ppm boron (Fig. 5(c)), the boron concentration is about 0.3 ppm, and strong absorption at 2800 cm^{-1} and other bands caused by the boron impurity are observed.

These results indicate that 1%-2% of the boron in the carbon source may be included in the grown diamond crystals. When high-purity graphite ($B < 0.1\text{ ppm}$) was used for the carbon source, colorless diamonds containing very small amounts of boron ($< 0.06\text{ ppm}$, undetectable level) were obtained (Fig. 5(a)). No absorption bands due to boron or nitrogen can be observed, in these colorless diamond crystals.

3.3. Inclusions

When a nitrogen getter such as Al or Ti is added to the solvent metal, the grown diamond is liable to trap inclusions. The major inclusions are solvent metals, which are incorporated in the crystal in a form like that shown in Fig. 6. This phenomenon of including the solvent metal is also observed when growing type Ib diamond (no addition of nitrogen getter) if the growth

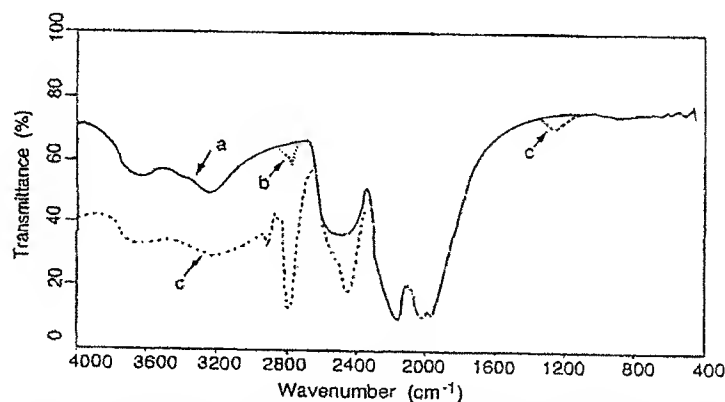


Fig. 5. IR spectra of diamonds grown using synthetic diamond powders containing (a) $< 1\text{ ppm}$ boron, (b) about 3 ppm boron and (c) about 30 ppm boron. The boron concentrations are estimated as (a) $\leq 0.06\text{ ppm}$, (b) about 0.1 ppm and (c) about 0.3 ppm .



Fig. 6. Metal inclusions in synthetic diamond grown with a nitrogen getter added to the solvent.

rate is too fast or the crystal growing process becomes unstable because of an accidental change in the growth conditions. When a nitrogen getter is added to the solvent, the solubility of carbon in the solvent is decreased or the diffusion (flux) of carbon in the solvent is prevented; consequently, the metal inclusions are more easily incorporated in the crystal. The amount and distribution of the metal inclusions vary depending on the accuracy of the control of the growth condition.

The behavior of the inclusions in the diamond crystals grown in our laboratory was investigated. We used a magnetic balance to measure the concentration of solvent metal inclusions. Fig. 7 shows the relation between the concentration of inclusions and their distribution. Metal inclusions tend to be trapped near the seed and distributed radially. When the concentration of inclusions is less than about 0.5 wt.%, they are located near the seed.

Fig. 8 shows the concentration of metal inclusions in diamond crystals which were grown at the same rate of about 2 mg h^{-1} as a function of the amount of Al or Ti added to the solvent. The concentration of metal inclusions increased with increasing amount of Al or Ti, and inclusions occurred more readily with Ti than with Al. In the case of Ti, in addition to metal inclusions, many fine inclusions of diameter more than $10 \mu\text{m}$ were also seen everywhere in the diamond crystal (Fig. 9). When a cross-section of the solvent metal was observed after diamond synthesis, many black spots with diameters ranging from a few micrometers to more than $10 \mu\text{m}$

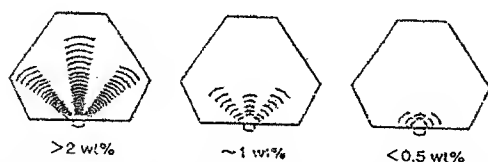


Fig. 7. Schematic drawings of metal inclusions in synthetic diamond.

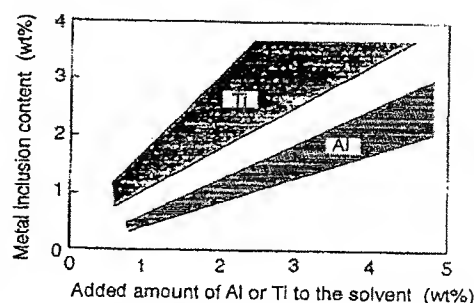


Fig. 8. Metal inclusion concentration in synthetic diamond versus the amount of Al or Ti added to the solvent.

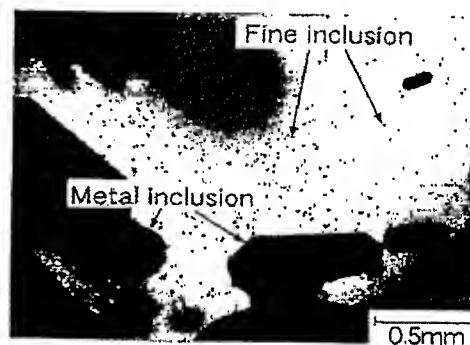


Fig. 9. Fine inclusions in synthetic diamond grown on adding Ti to the solvent.

were observed (Figs. 10(a-1) and 10(a-2)). The results of EPMA and X-ray diffraction analysis showed that these black spots were TiC. The TiC particles were mainly concentrated in the upper part of the solvent (Fig. 10(a-1)) and were sparse downside of the solvent (Fig. 10(a-2)), near the grown diamond crystal. Therefore the fine inclusions in the diamond crystals are considered to be TiC particles that had been formed in the solvent metal. It is thought that the formation of a large amount of TiC in the solvent inhibits the transfer and diffusion of carbon, thus reducing the amount of carbon supplied to the crystal growth surface and delaying growth along the crystal surface, making it easier for metal inclusions to be trapped. Trapping of the TiC particle itself in the diamond crystals is unavoidable. Because of these inclusions due to TiC, almost no high-quality diamond crystals can be obtained when Ti is used as the nitrogen getter even if the growth rate is reduced substantially. When Zr and Hf were used as nitrogen getters, large amounts of carbides formed even in the lower side of the solvent metal and many carbides were included in the grown diamond crystals.

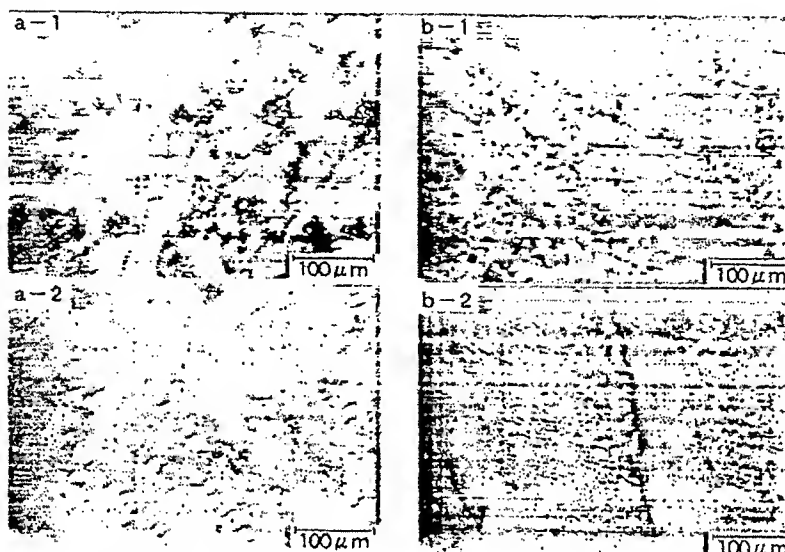


Fig. 10 Cross-section of the solvent metal after high-pressure and high-temperature treatment: (a-1) upper side and (a-2) lower side of the solvent with the addition of 1.5 wt.% Ti; (b-1) upper side and (b-2) lower side of the solvent with the addition of 1.5 wt.% Ti and 1.5 wt.% Cu.

3.4. Removal of the inclusions

When group IVA elements are used as nitrogen getters, almost all the nitrogen in the grown diamond is removed (<0.1 ppm), but many carbides form in the solvent, producing many inclusions in the growing crystals, and good-quality diamond crystals are very difficult to obtain.

In order to solve the inclusion problem, we added to the solvent materials that can decompose the carbides of the group IVA elements or suppress their formation. It is known that these carbides (e.g. TiC or ZrC) are decomposed in molten group Ib metals (Cu, Ag, Au etc.) [13]. Cu decomposes the carbides most effectively. Thereupon we added Cu to the solvent to suppress carbide (TiC) formation as well as adding Ti as a nitrogen getter.

Fig. 10(b) shows the surfaces of the cross-section of the solvent metal after high-pressure and high-temperature treatment when about 1.5 wt.% Ti and 1.5 wt.% Cu are added to the Fe+40Co solvent. The size of the TiC particles observed in the solvent (black spots) is reduced to $1\text{ }\mu\text{m}$ or less, and the amount is substantially decreased, particularly in the lower part of the solvent metal (Fig. 10(b-2)). The results indicate that TiC formation is suppressed or TiC particles are decomposed by the addition of Cu.

Diamonds were grown at a rate of 2 mg h^{-1} with varying amounts of Ti and Cu, and the content and distribution of inclusions in the diamond crystals were evaluated. Typical results are shown in Table 1. The

Table 1
Experimental results

added amount (wt%)		Grown diamond crystals		
		Nitrogen concentration (ppm)	Inclusions	
Ti	Cu		Metal (wt%)	Fine ^a
0.5	0.5	2.8	<0.5	—
1.0	—	0.3	1~2	+
1.0	1.0	0.3	<0.5	—
1.5	—	<0.1	1~2	+
1.5	1.5	<0.1	<0.5	—
2.0	—	<0.1	≥ 3	++
2.0	3.0	<0.1	~1	—

^aDegree of the fine inclusions: —, non; +, a few; ++, many.

amount of TiC particles (fine inclusion) decreased steeply on addition of Cu. This was accompanied by a decrease in metal inclusions, so that good-quality diamond crystals were synthesized. The efficiency of Ti with respect to the removal of nitrogen is not changed when Cu is added in amounts of 1–3 wt.%. However, a large excess of Cu causes metal inclusions.

Some diamond crystals were grown with the amounts of Ti and Cu fixed at 1.5 wt.% and the growth rate varied by changing the temperature difference. The concentration of the metal inclusions was measured with a magnetic balance. The results are shown in Fig. 11. By adding Cu and Ti, high-quality (inclusion-free) type IIa diamond crystals could be synthesized even at growth rates as high as $2\text{--}3\text{ mg h}^{-1}$. Some high-purity type IIa

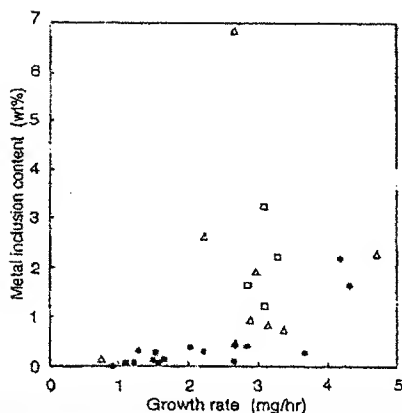


Fig. 11. Metal inclusion content of diamond crystals plotted against growth rate. The amount of nitrogen getter added is 1 wt.% Ti (Δ), 2 wt.% Ti (\square) and 1.5 wt.% Ti + 1.5 wt.% Cu (\bullet).



Fig. 12. High-purity synthetic type IIa diamond crystals prepared in this work.

diamond crystals of weight 1-2 carats grown by this method are shown in Fig. 12.

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